

Review

Invention of organotellurium and organostibine mediators for highly controlled degenerative transfer polymerization

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Abstract: Polymer-end mimetic organotellurium and organostibine compounds mediate highly controlled living radical polymerizations that allow the molecular weight to be controlled accurately and give well-defined end-groups. A variety of both conjugated (including styrene, acrylate and methacrylate derivatives) and unconjugated monomers (including 1-vinyl-2-pyrrolidinone and vinyl acetate) have been successfully polymerized in a controlled manner. The higher controllability of organotellurium- and organostibine-mediated polymerization compared to organoiodine-mediated polymerization is due to the faster degenerative transfer of organotellanyl and organostibino groups compared to iodine atom. AB-diblock, ABA-triblock and ABC-triblock copolymers have also been synthesized by the successive addition of different families of monomers. Transformations of the end-groups via radical and ionic reactions yielded polymers with a range of different functional groups and well-defined structures.

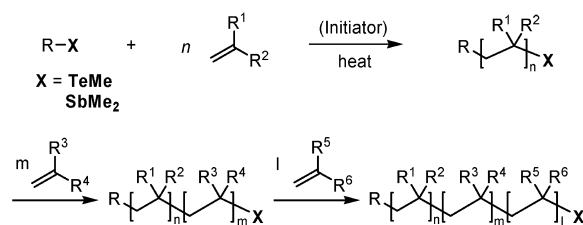
Key words: Living radical polymerization; radical coupling reaction; macromolecule synthesis; tellurium; antimony.

1. Introduction. Radicals are neutral, “soft”, and highly reactive species, and the conventional process of radical polymerization takes full advantage of these characteristics.¹⁾ Anion, cation, and coordination polymerizations usually require stringent reaction conditions to avoid the occurrence of undesirable side-reactions involving protic solvents, oxygen, and/or polar functional groups. In sharp contrast, radical polymerization can successfully take place in the presence of various polar functional groups, polar solvents including environmentally benign water, and impurities in the monomers. Furthermore, the high reactivity of radical species usually ensures that polymerization is completed at an ambient temperature, but with the disadvantage that the macromolecular structure of the polymer is difficult to control. Although this method has been widely used in the commercial production of polymeric materials,²⁾ conventional radical polymerization yields macromolecules that are polydisperse with a broad molecular weight distribution.

The development of living radical polymerization, by

analogy with the development of so-called living anion,³⁾ cation,⁴⁾ and coordination polymerizations,⁵⁾ has been a long-standing goal for synthetic polymer chemists. Significant advances have been reported during the past decade, and a variety of highly controlled and practical methods have been introduced.⁶⁾ Three representative methods, known as nitroxide-mediated radical polymerization (NMP),⁷⁾ atom transfer radical polymerization (ATRP)⁸⁾ and reversible addition-fragmentation chain transfer radical polymerization (RAFT),⁹⁾ are now widely used in the synthesis of a variety of advanced materials. However, the development of a more versatile process is needed in order to achieve the synthesis of different families of polymers with well-defined molecular structures and end-groups.

We have already reported that organotellurium compounds undergo reversible carbon-tellurium bond cleavage upon thermolysis and photolysis,¹⁰⁾ and that the resulting carbon-centered radicals can react with a variety of radical acceptors.^{11),12)} During the course of investigating new radical coupling reactions, we discov-



Scheme 1. General scheme of organotellurium- and organostibine-mediated living radical polymerization for the synthesis of homo polymer and di- and tri-block copolymers.

ered that organotellurium compounds promote living radical polymerization in a highly controlled manner.¹³⁾⁻¹⁶⁾ Mechanistic study of this process prompted us to develop a new living radical polymerization involving organostibines. A highly versatile method is reported here for the synthesis of structurally-defined polymers using organotellurium-mediated living radical polymerization (TERP)¹⁷⁾ and organostibine-mediated living radical polymerization (SBRP).¹⁸⁾ We have found that TERP and SBRP are extremely general processes that can be employed for the polymerization of different families of monomers in a highly controlled manner. Furthermore, the versatility of TERP and SBRP extends to the synthesis of various block copolymers starting from a single monofunctional mediator (Scheme 1).

2. Organotellurium-mediated living radical polymerization (TERP). *2-1. Homopolymerization of styrene.* We have already reported two experimental protocols by which TERP can successfully be conducted. In the first-generation procedure, organotellurium compounds and the monomer are heated at 80–110 °C.^{13),15)} For example, the bulk polymerization of styrene (100 equiv) was achieved by mixing mediator **1** with styrene and heating at 105 °C for 15 h. This resulted in the formation of polystyrene with the predicted molecular weight ($M_n = 9400$) for a given styrene/**1** ratio, and low polydispersity index (PDI = 1.15, Table I, entry 1). Much milder conditions were used in the second-generation procedure, where azo-initiators were added to the same reaction mixture.¹⁶⁾ The polymerization of styrene (100 equiv) with **1** was achieved by heating at 60 °C for 11 h in the presence of one equivalent of 2,2'-azobis(isobutyronitrile) (AIBN). Polystyrene of the desired molecular weight ($M_n = 11300$) and low polydispersity index (PDI = 1.17) was obtained in quantitative yield (Table I, entry 2). By using 2,2'-azobis(4-methoxy-2,4-dimethylvaleronitrile) (V-70), which gen-

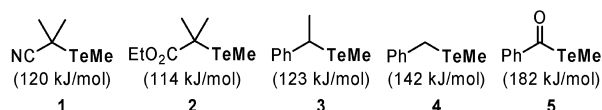


Fig. 1. Structure of organotellurium mediators used for living radical polymerization. The numbers in the parenthesis are bond dissociation energy obtained by the DFT calculation at (U)B3LYP/6-31G*+LANL2DZ(Te) level of theory.

erates radical species at lower temperatures than AIBN, well-defined polystyrene was synthesized at 40 °C (Table I, entry 3). Although the addition of azo-initiators might be expected to cause free radical polymerization, resulting in a loss of controllability, these results clearly indicate that such undesirable phenomena do not take place. The origin of the effects of adding azo-initiators will be discussed in Section 2-7.

The effects of varying the structure of the organotellurium mediator were examined (Fig. 1). Mediators **2** and **3** were able to control the polymerization of styrene regardless of whether AIBN was added, and polystyrenes with controlled molecular weights and low polydispersity were obtained in high yields (PDI = 1.15–1.18, Table I, entries 4–7). Conversely, synthesis using mediators **4** and **5** showed poor controllability, and polystyrenes with relatively high polydispersity indices were obtained (PDI = 1.46–1.58, Table I, entries 8 and 9). The calculated carbon-tellurium bond dissociation energies of mediators **1–5** are shown in Fig. 1. Mediators **1–3** possess similar bond dissociation energies, the values of which are considerably lower than those of **4** and **5**. This strongly suggests that the poorer control of polymerization on using **4** and **5** can primarily be ascribed to a slower rate of generation of carbon-centered radicals compared to mediators **1**, **2**, and **3**.

2-2. Confirmation of the living character of polymerization. The living character of the current polymerization was ascertained by several control experiments. First, the molecular weight (M_n) increased linearly with an increase of the conversion of styrene when polymerization was carried out with 100 equiv of styrene and **3** (Fig. 2). Second, the molecular weight (M_n) also increased linearly with an increase in the amount of styrene used (Table I, entries 10–13, and Fig. 3), although the experimentally determined molecular weight begins to deviate from the theoretical value as the targeted molecular weight increases ($M_n > 50000$). Despite this deviation, the obtained high-molecular-weight polystyrenes were monodisperse with an

Table I. Effects of organotellurium-promoters and azo-initiators in homopolymerization of styrene

Entry	Equiv	Promoter	Initiator ^b	Condns. (°C/h)	Yield (%)	M_n^c	PDI ^c
1	100	1	none	105/15	98	9400	1.15
2	100	1	AIBN	60/11	94	11300	1.17
3	100	1	V-70	40/23	82	7400	1.21
4	100	2	none	105/15	79	9000	1.15
5	100	2	AIBN	60/11	88	11500	1.18
6	100	3	none	105/16	96	9200	1.17
7	100	3	AIBN	60/11	91	9100	1.18
8	100	4	none	105/18	89	9000	1.46
9	100	5	none	105/18	83	25400	1.58
10	300	3	none	100/16	85	25200	1.22
11	500	3	none	100/19	78	29500	1.21
12	800	3	none	100/19	80	52600	1.30
13	1000	3	none	100/19	84	62600	1.37

^aA mixture of the promoter and styrene was heated without solvent. ^bOne equivalent of azo-initiator was used. AIBN: 2,2'-azobis(isobutyronitrile), V-70: 2,2'-azobis(4-methoxy-2,4-dimethylvalero-nitrile). ^cNumber-average molecular weight (M_n) and polydispersity index (PDI = M_w/M_n) were obtained by size exclusion chromatography calibrated by polystyrene standards or polyMMA standards. ^dOne equivalent of dimethyl ditelluride was added.

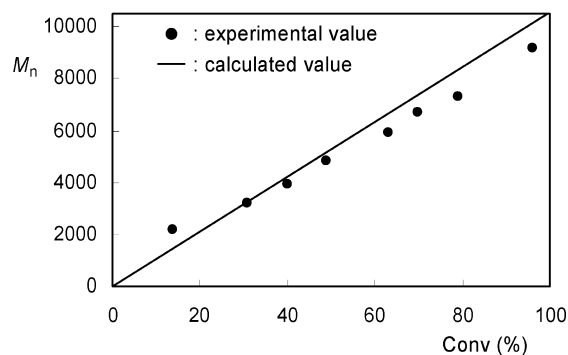


Fig. 2. Correlation of experimental and theoretical molecular weight (M_n) of polystyrene obtained by the bulk polymerization of styrene (100 equiv) with **3** as a function of the conversion of styrene.

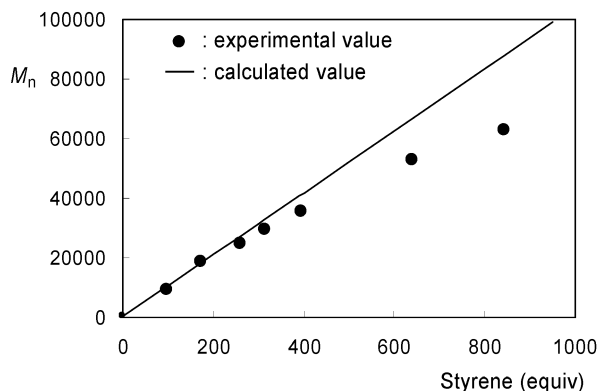


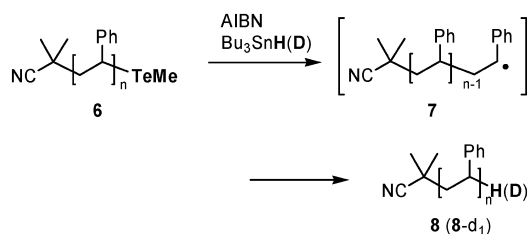
Fig. 3. Correlation of experimental and theoretical molecular weight (M_n) of polystyrene in the bulk polymerization of styrene with **3** as a function of the amount of styrene used (100-1000 equiv).

acceptable level of controllability.

Finally, the existence of an active carbon-tellurium bond in the polymer end-group was confirmed by labeling experiments. Thus, polymer block **6** prepared from **1** and 30 equiv of styrene was reduced quantitatively using either tributyltin hydride or tributyltin deuteride to yield the end-protonated or deuterated polystyrene **8** or **8-d₁** via the radical intermediate **7** (Scheme 2). Selective incorporation of the deuterium atom in the polymer was confirmed from MALDI-TOF mass spectroscopy by observing an increase of one mass number for **8-d₁** compared to **8** (Fig. 4). The ²H NMR spectrum of **8-d₁** further supported the selective incorporation of deuterium at the benzylic position ($\delta = 2.36$ ppm, broad singlet). These results clearly demonstrate the existence of the organotellurium polymer-end group, which was reduced to **8** by tributyltin hydride. Furthermore, the difference between the main mass peaks is 104, which corresponds to the molecular mass of styrene, and there are no significant peaks arising from impurities. These observations clearly demonstrate the highly controlled character of the TERP, in which the polymerization is initiated by a radical generated from **1** and proceeds in the absence of unfavorable side reactions.

2-3. Polymerization of functionalized monomers.

We have found that TERP is highly versatile and can control the radical polymerization of a variety of functionalized monomers (Table II).¹⁴⁾ Acrylate esters were successfully polymerized in a controlled manner by heating mediators **1-3** using the first-generation proce-



Scheme 2. Reduction of polymer-end methyltellanyl group with tributyltin hydride or deuteride.

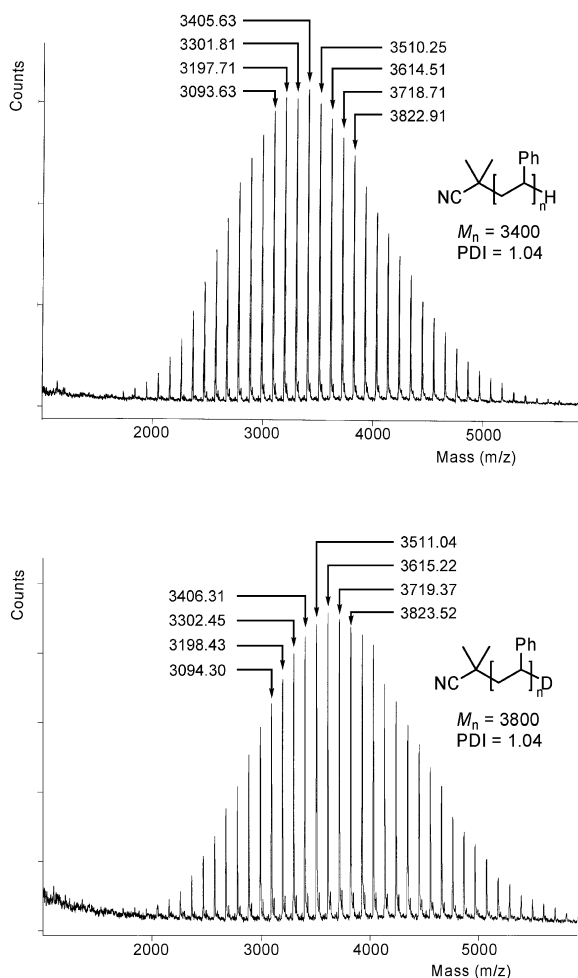


Fig. 4. The MALDI-TOF mass spectra of end-protonated and deuterated polystyrene **8** and **8-d₁**. The molecular ions were observed as silver ion adducts [$m/z = (M + \text{Ag})^+$]. Molecular weight (M_n) and polydispersity index (PDI) were directly obtained by MS.

ture (100 °C, no azo-initiators), regardless of the bulkiness of the pendant alkoxy groups (Table II, entries 1-5). Poly(acrylate esters) of the desired molecular weight and with low polydispersity indices (PDI = 1.11-1.18) were obtained in all cases. We also found that the addition of AIBN (the second-generation procedure) was remarkably effective in improving the required polymerization conditions.¹⁶⁾ Thus, the polymerization of *n*-butyl acrylate (nBA) was completed within 4 h at 60 °C when AIBN was added, while the first-generation procedure required heating for 24 h at 100 °C (Table II, entries 5 and 6). Although the polydispersity index increased from 1.13 to 1.17 on addition of AIBN, nevertheless a very high level of control was achieved.

We also examined the polymerization of methyl methacrylate (MMA, 100 equiv) with mediators **1** and **2**, but initial attempts revealed that the reaction was insufficiently controllable using the first-generation procedure at 80 °C (PDI = 1.37-1.77, Table II, entries 7 and 11). This problem could be attributed to the high reactivity of MMA toward the polymer-end radicals, and thus we anticipated that the addition of an agent to cap the radical species would enhance the controllability. We thought that ditellurides would serve as capping reagents for the polymer-end radicals, because they are known to be excellent radical capturing reagent.¹⁹⁾ Indeed, polyMMA with low polydispersity was obtained by the addition of one equiv of dimethyl ditelluride (PDI = 1.12-1.16, Table II, entries 8 and 12). Similar results were also obtained for mediator **3** in the presence of dimethyl ditelluride (PDI = 1.18, Table II, entry 13). In accordance with the living character of the current polymerization, the molecular weight increased linearly with the amount of MMA used, and precisely controlled high molecular-weight polyMMA was formed by the addition of one or two equiv of dimethyl ditelluride (Table II, entries 14-16). Use of the second-generation procedure, with the addition of AIBN and dimethyl ditelluride, resulted in complete polymerization after heating at 60 °C for 2 h, and afforded well-defined polyMMAs in excellent yields (Table II, entries 9 and 10).

Since TERP is performed under thermal conditions, without the need to add catalysts that are incompatible with the functionalities of the monomers, controlled polymerization of various monomers possessing functional groups can be achieved successfully using both first- and second-generation procedures. For example, the controlled polymerization of styrene derivatives possessing chloro and methoxy groups was successfully carried out (Table II, entries 17 and 18).

Table II. Polymerization of functionalized monomers by TERP

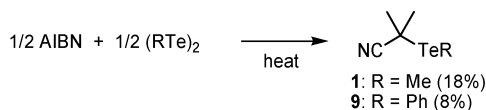
Entry	Monomer ^a (equiv)	Promoter	Initiator ^b	Condns. (°C/h)	Yield (%)	M_n^c	PDI ^c
1	MA (100)	2	none	100/24	70	6400	1.11
2	MA (100)	3	none	100/24	86	8800	1.12
3	tBA (100)	2	none	100/24	85	9800	1.18
4	nBA (100)	1	none	100/24	69	8300	1.12
5	nBA (100)	3	none	100/24	89	10300	1.13
6	nBA (100)	3	AIBN	60/4	94	10700	1.17
7	MMA (100)	1	none	80/13	74	8600	1.37
8	MMA (100)	1^d	none	80/13	81	8300	1.12
9	MMA (100)	1	AIBN	60/2	93	11000	1.36
10	MMA (100)	1^d	AIBN	60/2	98	9600	1.15
11	MMA (100)	2	none	80/15	67	11800	1.77
12	MMA (100)	2^d	none	80/13	84	8200	1.16
13	MMA (100)	3^d	none	80/13	92	9700	1.18
14	MMA (200)	3^d	none	80/19	83	16200	1.14
15	MMA (500)	3^e	none	80/18	79	36300	1.18
16	MMA (1000)	3^e	none	80/24	83	79400	1.14
17	ClSt	3	none	100/17	88	8800	1.41
18	MeOSt	3	none	100/36	94	10900	1.17
19 ^f	AN	3	none	100/24	53	20800	1.07
20 ^f	AN	3	AIBN	60/6	99	37800	1.16
21 ^f	DMAEA	3	none	100/96	81	12000	1.23
22	DMA	3	none	105/23	100	10100	1.22
23 ^f	NIPAM	3	AIBN	60/3	99	30600	1.09
24 ^f	HEMA	2^d	none	80/17	97	22300	1.18
25 ^f	HEMA	3^d	AIBN	60/2	90	22300	1.18

^a100 equiv of monomer was used. MA: methyl acrylate, nBA: *n*-butyl acrylate, tBA: *t*-butyl acrylate, MMA: methyl methacrylate, ClSt: *p*-chlorostyrene, MeOSt: *p*-methoxystyrene, DMAEA: 2-dimethylaminoethyl acrylate, DMA: *N,N*-dimethylacrylamide, AN: acrylonitrile, NIPAM: *N*-isopropylacrylamide, HEMA: 2-hydroxyethyl methacrylate. ^bOne equivalent of AIBN was used. ^cNumber-average molecular weight (M_n) and polydispersity index ($PDI = M_w/M_n$) were obtained by size exclusion chromatography calibrated by polystyrene standards or polyMMA standards. ^dOne equiv of dimethyl ditelluride was added. ^eTwo equiv of dimethyl ditelluride was added. ^fThe reaction was carried out in DMF.

These results are in sharp contrast to the copper-catalyzed ATRP process, in which *p*-methoxy-substituted styrene is a poor monomer due to the occurrence of a redox reaction with the catalyst.²⁰⁾ The successful polymerizations of acrylonitrile (AN), 2-dimethylaminoethyl acrylate (DMAEA), *N,N*-dimethylacrylamide (DMA) and *N*-isopropylacrylamide (NIPAM) are also noteworthy, since the polar functional groups of these monomers often hinder precise control of the polymerization when other methods are used (Table II, entries 19-23). Even 2-hydroxyethyl methacrylate (HEMA), which possesses a free hydroxyl group, could be successfully polymerized in a highly controlled manner in the presence of dimethyl ditelluride (Table II, entries 24 and 25).

2-4. *In situ* generation of mediators. Although the results described above were obtained using purified mediators, purification is not always necessary. We

have found that *in situ*-generated mediators can also be used for the controlled polymerization of a range of monomers.^{15),21)} By analogy with the high reactivity of ditellurides towards carbon-centered radicals, the thermal reaction of diazo compounds and ditellurides resulted in the formation of corresponding organotellurium compounds. For example, the reactions of equimolar quantities of AIBN with dimethyl ditelluride and diphenylditelluride produced mediators **1** and **9** in 18% and 8% yields, respectively (Scheme 3). The reaction mixture mainly consisted of 2,2,3,3-tetramethylsuccinonitrile, which was formed by coupling of the AIBN-



Scheme 3. *In situ* generation of organotellurium mediator from AIBN and ditellurides.

Table III. TERP with *in situ* generated mediators

Entry	Ditelluride ^a (R)	Method	Monomer ^b (equiv)	Condns. (°C/h)	Yield (%)	M_n^c	PDI ^c
1	Me	A	St	90/36	54	11700	1.20
2	Ph	A	St	80/56	55	19000	1.20
3	Me	A	BA	100/48	>3	2900	1.06
4	Ph	A	BA	100/24	25	19000	1.20
5	Me	A	MMA	80/13	95	28800	1.14
6	Ph	A	MMA	80/4	96	50100	1.22
7	Me	B	St	90/32	88	9200	1.38
8	Ph	B	St	90/45	93	6900	1.48
9	Me	B	BA	100/24	38	3400	1.10
10	Me ^d	B	BA	100/24	89	7800	1.24
11	Ph	B	BA	100/24	88	7200	1.18
12	Me	B	MMA	80/0.5	100	131300	1.55

^aOne equivalent with respect to AIBN was used. ^b200 equiv of monomer with respect to ditelluride was used. ^cNumber-average molecular weight (M_n) and polydispersity index (PDI = M_n/M_w) were obtained by size exclusion chromatography calibrated by polystyrene standards or polyMMA standards. ^d0.7 equiv with respect to AIBN was used.

derived radicals, together with unreacted ditelluride.

Despite these low coupling efficiencies, the *in situ* generation of both **1** and **9** was sufficient to mediate the controlled polymerization of subsequently added vinyl monomers (method A), although the efficiency and controllability of the reaction depended on the type of vinyl monomers used. The polymerization of MMA was most successful with this method; polyMMA products with low polydispersity indices and molecular weights as predicted by the ratio of generated mediator to monomers were obtained in high yield (Table III, entries 5 and 6). As the initial reaction mixture contained unreacted ditelluride, further addition of this compound was unnecessary. Styrene was slowly polymerized upon prolonged heating at 80–90 °C with a polydispersity index of 1.20, but conversion rates were moderate (Table III, entries 1 and 2). The polymerization of butyl acrylate was slow and was not completed within a practically useful time-scale, despite the very low polydispersity indices of the resulting polymers (Table III, entries 3 and 4). The slow reaction speed can be attributed to the existence of ditellurides in the reaction mixture, which shift the equilibrium from the polymer-end radicals to the dormant organotellurium species.

Alternatively, a one-step polymerization procedure mixing AIBN, ditelluride and vinyl monomers can also produce well-defined polymers (method B), an especially effective method for the controlled polymerization of butyl acrylate (Table III, entries 9–11). This is due to a decrease in the amount of ditelluride in the reaction mixture caused by a decrease in coupling between the

AIBN-derived radicals, which now react preferentially with butyl acrylate followed by the ditelluride to form dormant species. Complete polymerization was almost achieved by varying the AIBN/ditelluride ratio (Table III, entry 10), or by using diphenylditelluride (Table III, entry 11); the desired poly(butyl acrylate) products were formed, with low polydispersity indices (PDI < 1.24). The polymerization of styrene using method B was less controllable than that by method A (Table III, entries 7 and 8), and the polymerization of MMA could not be controlled at all (Table III, entry 12).

Both methods are simple to perform since both AIBN and ditellurides are stable in air and can be handled without special precautions, whereas promoters **1**–**3** are sensitive to oxygen and must be stored under an inert atmosphere and manipulated using standard syringe techniques. Despite the practical simplicity of these methods, the use of purified initiators is the method of choice to obtain polymers with the highest level of controllability in terms of molecular weight and polydispersity.

2-5. Block copolymer synthesis. A notable feature of the TERP is its versatility for the synthesis of block copolymers. While the success of block copolymer synthesis is in general highly dependent on the order of monomer addition, especially when different families of monomers are used, we have found that TERP is more tolerant towards the order of addition. For example, blocking of the polystyrene macromediator was successfully carried out for *p*-methoxystyrene (MeOSt), MMA, and *t*-buthyl acrylate (tBA), and the desired AB-

Table IV. Synthesis of AB di- and ABA tri- and ABC triblock copolymers using macroinitiators

Entry	Macroinitiator ^a (M_n /PDI)	Monomer (equiv)	Condns. (°C/h)	Yield (%)	M_n^b	PDI ^b
AB Diblock copolymer						
1	polySt (8800/1.17)	MeOSt (100)	105/11	58	18000	1.19
2	polySt (9000/1.15)	MMA (100) ^c	80/16	85	13900	1.25
3	polySt (9000/1.15)	tBA (100)	100/25	50	11300	1.18
4	polyMMA (8500/1.12) ^d	St (100)	100/24	85	18800	1.13
5	polyMMA (8500/1.12) ^d	tBA (100)	100/25	57	17100	1.11
6	poly(tBA) (9600/1.10) ^d	St (100)	100/36	77	19200	1.32
7	poly(tBA) (8200/1.19) ^d	MMA (100) ^c	100/18	88	19500	1.35
ABA Triblock copolymer						
8	poly(MMA- <i>b</i> -St) (18700/1.18)	MMA (200) ^c	80/24	65	28100	1.22
9	poly(MMA- <i>b</i> -tBA) (11000/1.11)	MMA (200) ^c	100/15	83	18600	1.30
ABC Triblock copolymer						
10	poly(St- <i>b</i> -MMA) (12600/1.30)	tBA (200)	100/22	32	16100	1.27
11	poly(MMA- <i>b</i> -St) (19000/1.13)	tBA (200)	100/24	45	21800	1.18
12	poly(MMA- <i>b</i> -tBA) (11500/1.09)	St (200)	100/15	69	21600	1.27

^aThe macroinitiator was prepared from mediators **3** and the corresponding monomer according to the conditions shown in Tables I and II. ^bMolecular weight (M_n) and polydispersity index (PDI) were determined by size exclusion chromatography calibrated by polystyrene standards. ^cOne equiv of dimethyl ditelluride was added. ^d M_n and PDI were calibrated by polyMMA standards.

diblock copolymers with low polydispersity indices were obtained in good to excellent yields in all cases (Table IV, entries 1-3). The addition of ditelluride was necessary when MMA was used as the second monomer, as is also the case for the homopolymerization of MMA (Table IV, entry 2). The controlled syntheses of AB-diblock copolymers starting from a polyMMA macromediator with styrene and tBA, or from a poly(tBA) macromediator with styrene and MMA, were also possible by the subsequent addition of a second monomer (Table IV, entries 4-7). In all cases, the desired diblock copolymers with low polydispersity indices were obtained. Due to the stronger carbon-tellurium bonds found in poly(tBA) dormant species compared to those found in polystyrene and polyMMA species, the controllability of diblock copolymers initiated by the poly(tBA) macromediator was slightly less efficient (Table IV, entries 6 and 7), but still at an acceptable level (PDI < 1.35).

As the order of monomer addition is less important in TERP compared to that in other living radical polymerization techniques, ABA and ABC triblock copolymers could also be prepared starting from diblock macromediators (Table IV, entries 8-12). Thus, the successive treatment of **3** with MMA and styrene yielded a poly(MMA-*b*-St) macromediator, which was further reacted with MMA to give the desired poly(MMA-*b*-St-*b*-MMA) triblock copolymer with a narrow molecular

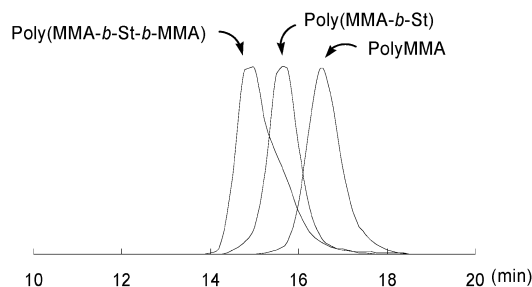
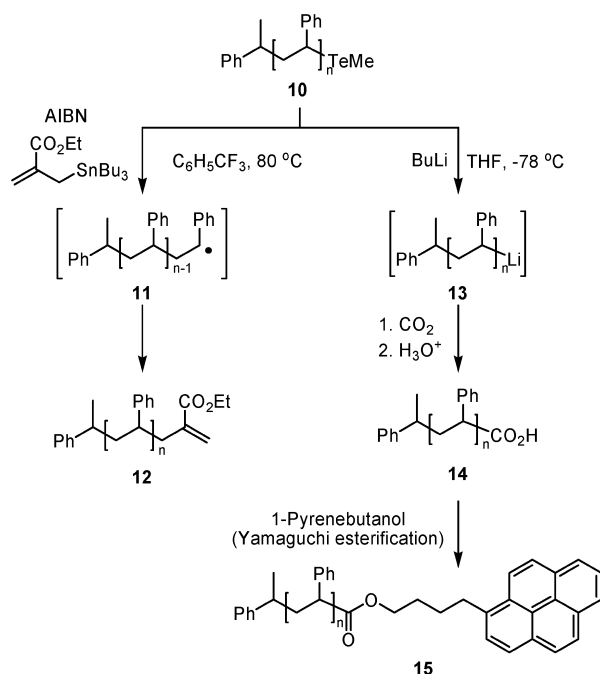


Fig. 5. GPC traces of the polyMMA, poly(MMA-*b*-St), and poly(MMA-*b*-St-*b*-MMA) block copolymers.

weight distribution (Table IV, entry 8). The GPC trace of the polymer at each stage of the synthesis clearly indicates the increase in molecular weight as the polymerization progresses (Fig. 5). An ABA triblock copolymer comprised of MMA and tBA could also be prepared using **3** by the successive polymerization of MMA, tBA and then MMA (Table IV, entry 9). Furthermore, ABC-triblock copolymers comprised of styrene, MMA, and tBA; of MMA, styrene, and tBA; and of MMA, tBA, and styrene could be synthesized by the successive addition of each monomer (Table IV, entries 10-12). These triblock copolymers were all obtained in a highly controlled manner with low polydispersity indices.

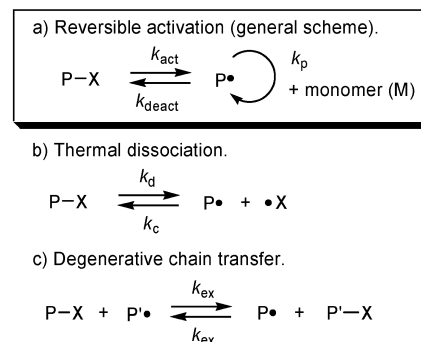
2-6. End-group transformations. Another char-

acteristic advantage of the TERP is the versatility of the transformations that can be carried out on the polymer end-groups (Scheme 4), since organotellurium compounds are excellent precursors for the generation of carbon-centered radicals,¹⁰⁾⁻¹²⁾ carbanions,²²⁾ and carbocations.^{23),24)} Thus, the treatment of polystyrene **10** with ethyl tributylstannylmethylacrylate produced the enoate-functionalized polymer **12** via polymer-end radical **11**, with 61% functionalization of the end group. Furthermore, tellurium-lithium transmetalation was achieved by the treatment of **10** with butyllithium. The resulting lithium species **13** could be trapped with carbon dioxide, giving carboxylic acid **14** after treatment with acid. The esterification of **14** with pyrenebutanol under standard Yamaguchi conditions²⁵⁾ yielded **15**, UV spectra of which revealed 86% incorporation of the carboxylate residue at the polymer end.



Scheme 4. Synthesis of end-modified polystyrenes.

2-7. Mechanism. All of the living radical polymerization reported so far proceed via three elementary steps, namely initiation, propagation, and deactivation (Scheme 5a).²⁶⁾ The dormant species P-X generates an active P radical, which reacts with the monomer(s) to give the chain-elongated polymer-end radical before deactivation to the dormant species takes place. A significant feature of the process of reversible radical generation is a decrease in the concentration of radical species in solution and the minimization of undesirable



Scheme 5. General mechanism of living radical polymerization.

side reactions, for example, disproportionation and homo-coupling reactions that give dead polymers. Furthermore, the rapid deactivation allows the propagation of polymer-chains with similar chain lengths.

Studies of the kinetics involved in the activation step of the styrene polymerization using TERP have revealed the existence of two mechanisms, namely thermal dissociation (Scheme 5b, X = TeMe) and degenerative chain transfer (Scheme 5c, X = TeMe).¹⁶⁾ At 60 °C, the first-order rate constant for the thermal dissociation k_d is $1.2 \times 10^{-5} \text{ s}^{-1}$, and the second-order rate constant for the degenerative transfer k_{ex} is $5.7 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$, indicating that the latter mechanism is the dominant pathway. Therefore, once the initiating radical species have been formed, they predominantly undergo the degenerative-transfer mediated polymerization reaction. In the first-generation procedure, the thermolysis of the organotellurium compounds is the mechanism of radical generation. The high temperatures and long reaction times required are due to slow generation of the carbon-centered radical from the dormant organotellurium species by thermolysis. Conversely, in the second-generation procedure the initiating radicals are created from azo-initiators under mild thermal conditions, and the polymerization proceeds exclusively via the degenerative transfer mechanism.

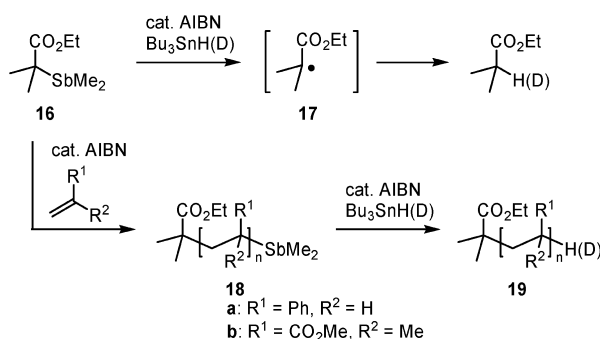
It is well known that a higher rate of degenerative transfer leads to greater control of the polymerization.²⁶⁾ The kinetics studies revealed that the rate of transfer of a methyltellanyl group at the polystyrene-end is approximately five times faster than that of an iodine atom.²⁷⁾ These results are consistent with the observation that TERP is more controllable than organoiodine-mediated living radical polymerization.²⁸⁾ Therefore, it has been demonstrated the importance of the choice of

heteroatom compounds in radical-mediated macromolecule synthesis.

3. Organostibine-mediated living radical polymerization (SBRP). The results of the kinetics studies discussed in Section 2-7 indicate that a high degree of control of the living radical polymerization process is made possible by an appropriate choice of heteroatom compounds. With the knowledge that tellurium, which lies immediately to the left of iodine in the periodic table, is a better heteroatom with respect to rapid degenerative transfer, we decided to focus on antimony, which lies immediately to the left of tellurium. Density functional theory calculations of simple model reactions initially suggest that organostibines are more reactive than organotellurides. The activation energies for the degenerative transfer of a methyl radical with trimethylstibine and dimethyltelluride were calculated to be 3.1 and 7.9 kJ/mol, respectively, at the B3LYP/6-31G*+LANL2DZ(Te,Sb) level of theory. Despite the intriguing possibilities suggested by these theoretical calculations, the use of organostibines as a source of carbon-centered radicals in synthesis has not been reported,²⁹⁾ and only a single example of the generation of carbon-centered radicals from organostibines has been reported thus far, being detected by an electron spin resonance spectroscopic study.³⁰⁾

By analogy with the organotellurium mediators, we synthesized the α -dimethylstibino ester **16** and examined the radical-mediated reduction with tributyltin hydride in the presence of AIBN as a proof-of-principle experiment for the generation of carbon-centered radicals from organostibines (Scheme 6). The reduction proceeded cleanly to give ethyl 2-methylpropanoate in quantitative yield. Replacement of the hydride by tributyltin deuteride gave the corresponding deuterated product. Furthermore, the reduction did not proceed in the presence of a radical inhibitor such as TEMPO. These results all provide evidence for the efficient generation of radical **17** from **16**.

We have found that **16** is also able to promote highly controlled living radical polymerization.¹⁸⁾ For example, the polymerization of styrene proceeded at 100 °C in the absence of azo-initiators, giving well-defined polystyrene with a predetermined molecular weight ($M_n = 7700$) and a low polydispersity index (PDI = 1.16) in good yield (Table V, entry 1). The rate of polymerization was increased considerably by the addition of AIBN (0.1 to 1.0 equiv), which also provided well-defined polystyrene with respect to molecular weight and polydispersity index (entry 2). The living character of the stib-



Scheme 6. Organostibine-mediated radical reduction and polymerization.

ine-based process was confirmed by the linear evolution of molecular weight with the amount of styrene used, and the fact that high-molecular-weight polystyrenes with low polydispersity indices were formed in all cases (entries 3 to 6). The existence of a dimethylstibino polymer end-group was determined by the TOF-MS and ²H NMR analyses of samples **19** and **19-d** ($R^1 = \text{Ph}$, $R^2 = \text{H}$) prepared by the tributyltin hydride- or deuteride-mediated radical reduction of the chain ends of living polystyrene **18a**.

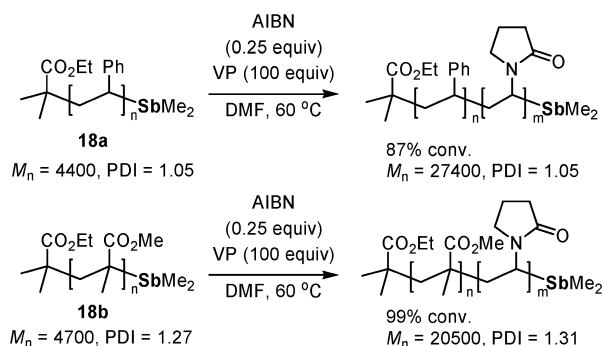
The most notable feature of the organostibine mediator is that it can control the polymerization of both conjugated and unconjugated vinyl monomers. Thus, organostibine **16** promoted the controlled polymerization of various conjugated monomers such as nBA, MMA, NIPAM and AN (entries 7-11), in addition to that of unconjugated monomers such as 1-vinyl-2-pyrrolidinone (VP)³¹⁾ and vinyl acetate (VA)³²⁾ (entries 12-15). In all cases we observed virtually complete conversion of the monomers within 1-18 h at 60 °C. The molecular weight of polyVP increased linearly with the amount of VP used, and the desired polymers were obtained with low polydispersity indices in all cases (entries 12-14). The organostibine-based technique is also compatible with a variety of polar functional groups. Consequently, the polymerization of NIPAM, AN and VP proceeded in a highly controlled manner and gave the desired polymers in excellent yields (entries 9-14).

We have also synthesized block copolymers from both conjugated and unconjugated monomers using the chain ends of a living polymer. The polystyrene and polyMMA macroinitiators **18a** ($M_n = 4400$, PDI = 1.05) and **18b** ($M_n = 4700$, PDI = 1.27), respectively, were treated with VP (100 equiv) in the presence of AIBN (0.25 equiv) in DMF at 60 °C for 8 h. We observed the essentially complete disappearance of the starting

Table V. Polymerization of functionalized monomers by SBRP^a

Entry	Monomer ^b (equiv)	AIBN (equiv)	Condns.	Yield (°C/h)	M_n^c (%)	PDI ^c
1	St (100)	none	100/48	82	7700	1.14
2	St (100)	0.5	60/19	99	8700	1.17
3	St (200)	0.5	60/24	99	15800	1.22
4	St (500)	0.5	60/36	76	25200	1.20
5	St (700)	0.5	60/36	76	41200	1.16
6	St (1000)	0.5	60/36	65	49400	1.23
7	BA (100)	0.3	60/1	96	12400	1.13
8	MMA (100)	0.3	60/4	100	11000	1.24
9 ^d	NIPAM (100)	0.1	60/12	99	13400	1.06
10 ^d	NIPAM (200)	0.3	60/12	99	26700	1.09
11 ^d	AN (100)	0.1	60/18	81	15000	1.05
12	VP (100)	0.5	60/0.5	99	10800	1.14
13	VP (300)	0.5	60/0.8	95	28600	1.18
14	VP (500)	0.5	60/1	92	42100	1.22
15	VA (25)	0.1	60/5	92	2800	1.26

^a A mixture of **1**, AIBN and monomer was heated under nitrogen atmosphere. ^b St: styrene, VP: 1-vinyl-2-pyrrolidinone, VA: vinyl acetate. ^c Number-average molecular weight (M_n) and polydispersity index (PDI) were obtained by size exclusion chromatography calibrated by polystyrene standards or polyMMA standards. ^d Reaction was carried out in DMF.



Scheme 7. Synthesis of diblock copolymers.

macromediators and the formation of the desired poly(St-*block*-VP) ($M_n = 27400$, PDI = 1.05) and poly(MMA-*block*-VP) ($M_n = 20500$, PDI = 1.31) in 87% and 99% yields, respectively (Scheme 7). These are the first reported examples of the successful block copolymerization of conjugated and unconjugated monomers. Such block copolymers are expected to be of great importance as functional organic materials with new or improved properties.³³⁾

Studies of the kinetics of styrene polymerization revealed that SBRP proceeds exclusively by the degenerative transfer mechanism. At 60 °C the rate constant for the thermal dissociation k_d approaches 0 s^{-1} , and the second-order rate constant for the degenerative transfer

k_{ex} is $1.1 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$. Therefore, while the thermal generation of carbon-centered radicals is negligible with the SBRP, the rate of transfer of the dimethylstibino group is approximately twice that of the methyltellanyl group in the TERP. Since a higher rate constant for degenerative transfer leads to a lower polydispersity index, SBRP is, in principle, better than TERP in terms of controlling molecular weight. Indeed, the organostibine compound enabled the polymerization of MMA to be controlled (entry 8), in contrast to the structurally related organotellurium compound which required the addition of ditelluride.

In Summary, organotellurium and organostibine compounds mediate highly controlled living radical polymerization to give structurally well-defined macromolecules. TERP and SBRP can be successfully performed on both conjugated and unconjugated vinyl monomers under similar conditions and with a high degree of control, and both techniques can tolerate monomers containing many different types of functional groups. Furthermore, a variety of AB-, ABA-, and ABC-block copolymers with well-defined structures can be prepared using the living end of the macromediators. The living end can also take part in further reactions to give end-modified polymers. These features clearly demonstrate the higher versatility of TERP and SBRP compared to other living radical polymerization methods

for the synthesis of functionalized macromolecules with well-defined structures.

Studies of the kinetics of living radical polymerization have revealed that the rates of the radical-mediated atom- or group-transfer reactions depend greatly on the identity of the heteroatom centers. The transfer of the dimethylstibino group is slightly faster than that of the methyltellanyl group, which is in turn considerably faster than the transfer of iodine atom. This is the origin of the higher degree of controllability enjoyed by SBRP and TERP compared to organoiodine-mediated radical polymerization. It is well known that the rate of degenerative transfer for halogen atoms and chalcogen species increases on going down the periodic table group; thus, organotellurides and organoiodides show the highest reactivities among group 16 and 17 compounds.³⁴⁾ However, until now little information has been reported on the reactivity of group 15 heteroatom compounds towards radicals, and also for the differences in reactivity among group 15, 16, and 17 heteroatom compounds across the same period.^{12c),34)} Therefore, our results demonstrate the importance of the choice of heteroatom in highly controlled radical-mediated synthetic reactions.

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